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# Presidential Green Chemistry Challenge Awards Program: Summary of 2016 Award Entries and Recipients



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# Presidential Green Chemistry Challenge Awards Program: Summary of 2016 Award Entries and Recipients

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## *Introduction*

Each year chemists, engineers, and other scientists from across the United States nominate their technologies for a Presidential Green Chemistry Challenge Award. This prestigious award highlights and honors innovative green chemistry technologies, including cleaner processes; safer raw materials; and safer, better products. These awards recognize and promote the environmental and economic benefits of developing and using novel green chemistry.

The U.S. Environmental Protection Agency (EPA) celebrates this year's innovative, award-winning technologies selected from among scores of high-quality nominations. Each nomination must represent one or more recently developed chemistry technologies that prevent pollution through source reduction. Nominated technologies are also meant to succeed in the marketplace: each is expected to illustrate the technical feasibility, marketability, and profitability of green chemistry.

Throughout the 21 years of the awards program, EPA has received 1,714 nominations and presented awards to 109 winners. By recognizing groundbreaking scientific solutions to real-world environmental problems, the Presidential Green Chemistry Challenge has significantly reduced the hazards associated with designing, manufacturing, and using chemicals.

Each year our 109 winning technologies are together responsible for:

- Reducing the use or generation of 826 million pounds of hazardous chemicals
- Saving 21 billion gallons of water
- Eliminating 7.8 billion pounds of carbon dioxide releases to air

And adding the benefits from the nominated technologies would greatly increase the program's total benefits.

This booklet summarizes entries submitted for the 2016 awards that fell within the scope of the program. An independent panel of technical experts convened by the American Chemical Society Green Chemistry Institute® judged the entries for the 2016 awards. Judging criteria included health and environmental benefits, scientific innovation, and industrial applicability. Five of the nominated technologies were selected as winners and were nationally recognized on June 13, 2016, at an awards ceremony in Portland, OR.

Further information about the Presidential Green Chemistry Challenge Awards and EPA's Green Chemistry Program is available at [www.epa.gov/greenchemistry](http://www.epa.gov/greenchemistry).

Note: The summaries provided in this document were obtained from the entries received for the 2016 Presidential Green Chemistry Challenge Awards. EPA edited the descriptions for space, stylistic consistency, and clarity, but they were not written or officially endorsed by the Agency. The summaries are intended only to highlight a fraction of the information contained in the nominations. These summaries were not used in the judging process; judging was based on all information contained in the entries received. Claims made in these summaries have not been verified by EPA.



# Academic Award

## *Catalysis with Earth Abundant Transition Metals*

**Professor Paul J.  
Chirik, Princeton  
University**

### **Innovation and Benefits**

Hydrosilylation is a chemical process that is critical for the production of a wide range of consumer goods. It relies on some of the least abundant elements in the Earth's crust, which results in high cost and significant environmental consequences. Professor Chirik discovered a new class of hydrosilylation catalysts based on earth abundant transition metals such as iron and cobalt that have superior performance to existing platinum catalysts.

Metal-catalyzed chemical reactions have enabled many of the technological innovations of modern society with applications ranging from the synthesis of advanced materials to new medicines. For decades, catalyst technology has relied on some of the least abundant elements in the Earth's crust – palladium, platinum, rhodium, and iridium. In addition to their high cost, price volatility, and toxicity, extraction of these elements has significant environmental consequences. Obtaining one ounce of a precious metal, for example, often requires mining approximately 10 tons of ore which creates a CO<sub>2</sub> footprint that is estimated to be 6,000 times that of abundant metals such as iron.

Alkene hydrosilylation is an example of a metal-catalyzed chemical reaction that is used on an industrial scale in the manufacture of silicones from alkenes and silanes. Silicones are found in a range of consumer products including adhesives, household utensils, medical devices, health care products, and low rolling resistance tires. The platinum catalyst used in alkene hydrosilylation reactions is often not recovered, however, which results in a significant environmental footprint for this commercially important process.

Professor Chirik and his research group, in collaboration with Momentive Performance Materials, discovered a new class of hydrosilylation catalysts based on earth-abundant transition metals such as iron and cobalt that have superior performance to existing platinum catalysts. This base metal catalyst technology offers the opportunity to enable new chemical processes that provide the desired product exclusively, eliminate distillation steps, and avoid generation of byproducts and unnecessary waste. This technology is based upon “metal-ligand cooperativity,” a broad catalysis concept pioneered by the Chirik group, where electron changes occur concomitantly between the metal and the supporting ligand.

Hydrosilylations to produce various commercial silicone products have been conducted on multi-gram scales using this new technology. The discovery of these air-stable, readily-synthesized iron and cobalt catalysts with unprecedented activity and selectivity may ultimately transform the industrial approach to commercial silicone products.

# Small Business Award

Verdezyne

## *Renewable Nylon through Commercialization of BIOLON™ DDDA*

### **Innovation and Benefits**

Dodecanedioic acid (DDDA) is used to manufacture nylon 6,12 for high performing engineered plastics, as well as in numerous other applications. DDDA is traditionally produced from petrochemicals via a multi-step chemical process using heat and nitric acid. Verdezyne developed a technology platform for producing BIOLON™ DDDA and other industrial chemicals from biobased and renewable raw materials.

Verdezyne developed a yeast fermentation technology platform to provide manufacturers and consumers with renewable alternatives to existing petroleum-based chemical intermediates. This technology focuses on the production of dicarboxylic acid chemical intermediates such as adipic acid, sebacic acid and dodecanedioic acid (DDDA). The first of these to be commercialized will be BIOLON™ DDDA, which will be used primarily in the manufacture of nylon 6,12 for engineered plastics that require special properties such as high chemical, moisture, or abrasion resistance. Other uses for DDDA are in the manufacture of adhesives, coatings, corrosion inhibitors, lubricants, and fragrances.

The current global demand for DDDA is estimated to be 100 million pounds per year. All DDDA currently on the market is produced from fossil-based sources, with the largest volume manufactured via trimerization of butadiene, followed by hydrogenation and oxidation with nitric acid. Verdezyne's process for production of BIOLON™ DDDA uses fatty acid feedstocks sourced from the co-products of vegetable oil refining as the starting raw material. In addition to providing a renewable alternative, this process offers a higher level of manufacturing safety since high temperature and pressure and concentrated nitric acid are no longer needed. Moreover, Verdezyne's process also results in reduced greenhouse gas emissions.

Verdezyne's production of BIOLON™ DDDA is an aerobic fermentation process integrated with downstream product isolation and crystallization. The fermentation converts the twelve carbon fatty acid, lauric acid, to DDDA through the activity of Verdezyne's proprietary, genetically engineered *Candida sp.* yeast. The biochemical pathway involved is the three-step  $\omega$ -oxidation pathway that sequentially oxidizes the terminal end of an alkane (or a fatty acid) to a carboxylic acid. Verdezyne scientists specifically engineered this yeast to enable rapid, high-yield production of DDDA while minimizing the accumulation of pathway intermediates that can be toxic to the organism and detrimental to final product purity.

Verdezyne's proprietary method for producing renewable BIOLON™ DDDA has been successfully demonstrated on a larger scale, enabling the production of over 70,000 pounds thus far. The product has met all industry quality specifications and has also earned the USDA Certified Biobased product label. The company's first commercial production facility is scheduled to open in 2017.



# Greener Synthetic Pathways Award

CB&I; Albemarle

## *AlkyClean® Technology: An Inherently Safer Technology for the Production of Gasoline Alkylate*

### **Innovation and Benefits**

Alkylate is a clean gasoline component and is produced from light olefins and isobutane. Despite being a cleaner product, traditional alkylate production uses toxic and corrosive liquid acid catalysts. CB&I, Albemarle, and Neste developed an inherently safer solid acid catalyst alkylation technology that produces gasoline alkylate with a lower environmental impact.

Alkylate is a highly valued “clean fuels” blending component for motor gasoline. It consists of clean-combusting isoparaffins that have low vapor pressures and high octane values. Alkylate also does not contain toxic components such as aromatics, olefins, or sulfur compounds. Alkylate is the preferred gasoline blending component for compliance with relevant environmental regulations.

Alkylate is produced from the reaction of isobutane and light olefins (C3-C5). Alkylate production is currently about 30 billion gallons/year worldwide, of which 60% is located in North America. A challenge facing refineries today is that alkylate production requires the use of liquid acid catalyzed processes, typically hydrofluoric acid or sulfuric acid. Hydrofluoric acid, in particular, is extremely toxic and, upon release, forms clouds that can be lethal for up to five miles.

For more than 40 years, scientists have been trying to replace liquid acid technologies with a greener solid acid catalyst technology. Prior approaches failed because of poor product selectivity and/or excessively rapid catalyst deactivation, coupled with the lack of an acceptable catalyst regeneration procedure. In some cases, these catalysts used leachable corrosive components such as halogens, triflic acid, and boron trifluoride, which could migrate into product streams.

Albemarle and CB&I developed a catalyst-process combination technology, the AlkyClean® solid acid alkylation process, which coupled with CB&I’s novel reactor scheme, produces high quality alkylate without the use of liquid acid catalysts. Additionally, neither acid-soluble oils nor spent acids are produced, and there is no need for product post-treatment of any kind.

Albemarle’s AlkyStar™ catalyst was designed for use exclusively with the AlkyClean® alkylation process. It uses a type of zeolite catalyst that is well-proven in the industry. The strength and the number of acid sites on the catalyst have been optimized to enhance hydrogen transfer reactions over multiple alkylation reactions. The catalyst particle size and porosity were also optimized using a pilot plant and a demo unit that allowed the investigation of regeneration procedures as well.

The world’s first commercial-scale, solid catalyst alkylation unit was started up in August, 2015. The unit employs the AlkyClean® technology and has a capacity of 2,700 BPD alkylate production. The plant has met or exceeded all performance expectations and is producing an alkylate product of quality that is on par with existing technologies.

## **Greener Reaction Conditions Award**

### *Instinct<sup>®</sup> Technology – Making Nitrogen Fertilizers Work More Effectively for Farmers and the Planet*

#### **Innovation and Benefits**

Agricultural activity introduces a significant amount of nitrate into ground and surface waters. Dow Agrosciences developed Instinct<sup>®</sup> nitrogen stabilization technology which protects nitrogen fertilizer in the ammoniacal form, thereby reducing nitrate leaching to ground and surface waters as well as atmospheric nitrous oxide emissions. Instinct<sup>®</sup> also results in longer retention of applied nitrogen in a plant's root zone for optimal crop utilization and yield.

The demand for higher crop yields and agricultural productivity is ever increasing, and so are concerns for the negative impacts on the environment caused by agricultural activities. Human activities related to farming account for a significant percentage of nitrate in ground and surface waters as well as nitrous oxide emissions. An estimated 75% of all nitrous oxide emissions, for example, come from agricultural activities such as applied nitrogen fertilizers and manures.

Crop genetics and precision application methods have improved the efficiency of applied nitrogen fertilizers, but losses to the environment are still significant after soil bacteria quickly convert nitrogen from the applied urea or ammoniacal form to nitrate. In the nitrate form, nitrogen fertilizer is susceptible to losses through leaching or as emissions in the form of nitrous oxide. Furthermore, nitrate fertilizer that leaches out of a plant's root zone is no longer available to provide nutrients to the crop.

Scientists at The Dow Chemical Company discovered a powerful nitrification inhibitor that can inhibit soil bacteria from rapidly converting nitrogen in the ammoniacal form to nitrate, thereby retaining more nitrogen in the more stable ammoniacal form. By keeping nitrogen in the root zone for a longer period during the season, Dow's nitrogen stabilizers improve Nitrogen Use Efficiency and reduce nitrogen loss through leaching and nitrous oxide emissions. N-Serve<sup>®</sup> was the first commercial product introduced by Dow in 1974, but it is only suitable for use with anhydrous ammonia fertilizer applications due to the limitations of its physical-chemical properties.

In 2010, Dow AgroSciences launched a novel, aqueous microcapsule suspension product, Instinct<sup>®</sup>. This patented technology can be conveniently used with other commonly used nitrogen fertilizer sources, enabling adoption of the product for multiple crops in the U.S. and around the world. As an aqueous suspension of a microencapsulated active ingredient, Instinct<sup>®</sup>, also provides additional environmental benefit by significantly reducing the amount of petroleum-based solvents used per treated acre.

In less than five years, acres treated with stabilized nitrogen have grown more than five-fold. In 2014 alone, based on calculated adoption of Instinct<sup>®</sup> in the U.S., it is estimated that use of the technology reduced carbon dioxide equivalent emissions by about 664,000 metric tons and increased U.S. corn production by about 50 million bushels, equating to about \$205,500,000 additional production revenue for U.S. corn growers.

# Designing Greener Chemicals Award

## Specific Environmental Benefit: Climate Change Award

**Newlight  
Technologies**

### *AirCarbon: Greenhouse Gas Transformed into High-Performance Thermoplastic*

#### **Innovation and Benefits**

Fossil fuels are refined, cracked, and then polymerized at high temperature and pressure in petro-based processes to make plastics. Newlight Technologies developed a technology that produces high performance, carbon-negative AirCarbon™ resins from captured greenhouse gases. AirCarbon™ uses a proprietary biocatalyst to produce plastics at lower cost compared to plastics from petrochemicals.

Methane is emitted by natural sources such as wetlands. It is also the second most prevalent greenhouse gas emitted in the U.S. from human activities, such as leakage from natural gas systems and the raising of livestock. Methane's lifetime in the atmosphere is much shorter than carbon dioxide, but methane is more efficient at trapping radiation. Pound for pound, the comparative impact of methane on climate change is more than 25 times greater than carbon dioxide over a 100-year period.

Newlight Technologies developed and commercialized a carbon capture technology that combines methane with air to produce AirCarbon™, a high-performance thermoplastic material that matches the performance of a wide range of petroleum-based plastics while out-competing on price. Newlight's biocatalyst combines air and methane-based carbon to produce polymers at environmentally friendly, ambient conditions. Despite the conceptual simplicity, previous technologies utilizing carbon capture to manufacture plastics resulted in production costs that were significantly higher than petroleum-based manufacture of plastics.

To overcome this long-standing cost challenge, Newlight developed a biocatalyst that does not "turn itself off" based on the amount of polymer being produced. To do this, Newlight developed a process to disable the negative feedback receptors on polyhydroxyalkanoate polymerase, the central polymer production enzyme in the biocatalyst. As a result, the biocatalyst is able to continue to polymerize significantly beyond previous maximum limits and generate a yield of nine kilograms of polymer for every one kilogram of biocatalyst (9:1) – nine times more material compared to previous technologies. Newlight's AirCarbon™ technology also reduces unit operations by a factor of three and capital cost by a factor of five, resulting in a net operating cost that enables AirCarbon™ to be cost and performance advantageous compared to petrochemical incumbents.

Within 24 months of scaling in 2013, AirCarbon™ was adopted by a range of leading companies including Dell, Hewlett-Packard, IKEA, KI, Sprint, The Body Shop, and Virgin to make packaging bags, containers, cell phone cases, furniture, and a range of other products. These products use a greenhouse gas in a carbon-negative process as a cost-effective replacement for petroleum-based plastics.



## Entries from Academia

### *Catalytic Couplings Mediated by Non-Precious Metal Catalysis*

This technology involves one of the most important classes of organic reactions used in modern research: namely, transition metal-catalyzed coupling reactions. These reactions are amongst the most effective and widely used means of constructing carbon–carbon (C–C) and carbon–heteroatom (C–X) bonds. The importance of cross-coupling methodology is underscored by the 2010 Nobel Prize given “for palladium-catalyzed cross-couplings in organic synthesis.” These couplings have transformed the landscape of chemical synthesis.

Despite the impact of palladium chemistry, there has been tremendous interest by academic and industrial researchers to develop related couplings that utilize non-precious metals. The Garg laboratory has focused on nickel catalysis, given that nickel is significantly more abundant, much less expensive, less toxic, and also possesses a much lower CO<sub>2</sub> footprint compared to palladium. Additionally, the American Chemical Society Green Chemistry Institute®’s Pharmaceutical Roundtable has prompted the development of coupling reactions that proceed in greener solvents. The use of non-precious metals or the use of greener solvents in popular coupling reactions each represents contemporary challenges in source reduction.

The Garg laboratory has reached four key milestones in the development of new nickel-catalyzed methodologies: (1) the nickel-catalyzed Suzuki–Miyaura coupling of aryl pivalate esters, carbamates, and sulfamates using C–O bond activation; (2) the cross-coupling of a range of aryl electrophiles using nickel catalysis in greener solvents; (3) the development of an undergraduate educational laboratory focused on “green” cross coupling reactions; and (4) the activation of traditionally “inert” amide C–N bonds for the synthesis of esters and ketones. In addition to providing greener alternatives to popular palladium-catalyzed reactions, the methodologies unveil new avenues of chemical reactivity.

### *Surface Engineered High-performance Catalysts for Fuel Cell Applications*

With exceedingly fast population and economic growth, the 21<sup>st</sup> century is met by enormous energy demand and environmental challenges. Meeting these needs is only possible with development of new energy resources, improved utilization efficiency of existing energy resources, and with reduced environmental impact. Catalysis has become a key in solving these challenges.

The operation of fuel cells, for example, relies on the dissociation of covalent bonds of hydrogen and oxygen on the catalyst surface to enable controlled redox reactions. Proton exchange membrane fuel cell is a promising clean energy technology for many applications, most notably for replacing the internal combustion engine in vehicles and generating zero emission. The U.S. Department of Energy determined an annual revenue of \$785 million in 2012 for fuel cell industries and estimates an increase in the number of fuel cell electric powered vehicles by a factor of ten until 2020. To become competitive with combustion engines, the current cost per kW using fuel cell technology of \$45/kW needs to be lowered to \$30/kW. Major obstacles towards reaching this goal are the limited efficiency of the oxygen reduction reaction (ORR) on the surface of fuel cell anodes and the low durability and high price of precious metals such as platinum (Pt).

The Huang laboratory recently demonstrated that by introducing a small amount of a third transition metal onto the surface layers of Pt<sub>3</sub>Ni octahedral nanocatalysts, highly active and exceptionally stable nanocatalysts (e.g., Mo–Pt<sub>3</sub>Ni/C) can be created with record high performance toward ORR, marking an important milestone in fuel cell development. The Huang laboratory is working closely with automobile companies to commercialize this technology for the broad applications in fuel cell vehicles with zero emissions and greatly reduced environmental impacts.

**Professor Neil Garg, Department of Chemistry and Biochemistry, University of California, Los Angeles**

**Professor Yu Huang, University of California, Los Angeles**

## *Replacing Packaging Plastics with Sustainable Bioplastics from Megacrop Waste*

This nominated technology describes the polymerization of abundantly available biogenic feedstocks—from lignin or lignocellulose—for the synthesis of novel polyesters suitable to replace environmentally unsound commodity packaging plastics such as polyethylene terephthalate (PET), polyvinylchloride (PVC), or polystyrene (PS). With readily tunable properties, these copolyesters are sustainable replacements for a variety of fossil fuel-based and non-degradable commodity plastics. Thus, they decrease reliance on finite petroleum and natural gas feedstocks, while ameliorating both the terrestrial trash crisis and the worsening ocean plastics catastrophe. This technology improves upon the most successful green polymer, polylactic acid (PLA), for several reasons: (1) the plastic deformation temperature can be finely tuned in the range of 78°C to 153°C, easily exceeding the value for PLA (55°C) and the values for PET (67°C), PVC (82°C), and PS (100°C); (2) these polymers are biodegradable and also water-degradable, affording benign or even diet-beneficial degradation byproducts; and (3) the building blocks are abundant and scalable bioaromatics (vanillin, ferulic acid, or coumaric acid) that are sourced from non-edible forestry or megacrop wastes rather than edible biomass. Commercialization is pursued by U.S. Bioplastics, LLC, a start-up company presently designing a pilot plant to valorize the world's largest point-source of sugarcane bagasse, located in south Florida.

## *Highly Efficient and Practical Monohydrolysis of Symmetric Diesters*

Water is the least expensive solvent and among the most environmentally friendly solvents because it generates no hazard during chemical conversion processes unlike organic solvents. Water-mediated organic reactions replacing organic solvents thus represent a typical “green chemistry.” Among various synthetic conversions, desymmetrization of symmetric compounds is one of the most atom-economical and cost-effective reactions because the starting symmetric compounds are typically obtained easily on a large scale from inexpensive sources, or are commercially available inexpensively. Therefore, water-mediated desymmetrization of symmetric organic compounds is of tremendous synthetic value, and makes a significant contribution to creating greener reaction conditions.

Dr. Niwayama pioneered water-mediated desymmetrization. In particular, she has been developing monohydrolysis of symmetric diesters as the water-mediated desymmetrization reaction. Half-esters, which are produced by such monohydrolysis of symmetric diesters, are versatile building blocks in organic synthesis, applied to synthesis of polymers and dendrimers with applications to industrial products of commercial value. Since the two ester groups in symmetric diesters are equivalent, the statistically expected yield of half-esters would be a maximum of only 50%. Classical saponification usually affords complex mixtures of dicarboxylic acids, half-esters, and the starting diesters, which are difficult to separate, yielding a large amount of undesirable dirty waste. Ring-opening reactions of cyclic acid anhydrides require hazardous organic solvents. However, Dr. Niwayama discovered a highly efficient and practical ester monohydrolysis of symmetric diesters. In this reaction, an aqueous base such as NaOH or KOH is added to a symmetric diester suspended in water at 0°C. With this simple reaction, pure half-esters are obtained in high to near-quantitative yields without production of dirty waste and without use of hazardous organic solvents. This reaction, which is anticipated to significantly contribute to green chemistry, was licensed by three companies, and several half-esters produced by this reaction were commercialized.

# Entries from Small Businesses

## *New Chemical Impedes Biofilm Formation and the Adhesion of Foulers*

**Aequor, Inc.**

Aequor's products are novel, synthesized molecules that mimic natural marine chemicals. They effectively inhibit the ability of industrial and medical bacteria and fungi to attach to surfaces and colonize, and also remove the resulting biofilm and fouling. The molecules in Aequor's portfolio are all novel, scale-up ready, cost-effective to produce (synthesized in four steps), and effective at no or low toxic concentrations. Their molecular structures are simple for easy incorporation in multiple delivery systems (sprays, washes, pastes, paints, coatings, etc.). They are stable with a long shelf-life in powder form for reconstitution in liquid when needed. They are also potent, and can be used alone to replace toxic biocides (antimicrobials, antifouling agents, antiseptics, antibiotics) or in combination with them at lower concentrations. This can reduce the toxic load of hundreds of millions of tons of biocides (over 36 million tons annually of antifouling agents from the marine paint industry alone) that accumulate and persist in ecosystems and organisms. Aequor is accepting licensing proposals from market leaders that manufacture antibacterial and antifouling end-use products in each target sector: agro-industrial, consumer, medical, and defense. Aequor's new chemicals promise to save end-users time, manpower, and money by reducing: (1) the quantities and frequency of biocidal applications needed to control bacteria, microfouling, and macrofouling; (2) the costs of HAZMAT protocols for transport, storage, use and disposal of toxic agents that are flammable and with high explosion potential; and (3) up to 50% of fuel consumption and noxious gas emissions in industries (e.g., maritime transportation, water treatments, energy, etc.) where current antifouling paints and treatments have failed. On the medical side, Aequor's active agents are validated to reduce and eliminate infection caused by Gram-negative and Gram-positive bacteria.

## *Plating on Plastic*

**Alliance Finishing**

The need for plating on plastic was driven by lighter material requirements for use in automotive industry. Current processes use chromic acids and other toxic materials. There were various patents awarded for ABS-PC (acrylonitrile butadiene styrene-polycarbonate) plastics, however, still most use variants of other hazardous/toxic chemicals to achieve the surface modifications needed for metallization. Given the volumes of cars produced, along with other industries like medical, space, aerospace, defense, and pharmaceutical, the amount of waste streams generated is enormous. Chemicals such as chromic acids, permanganates, formaldehydes, solvents, and a host of others need to be manifested, rendered inert, and if possible, stabilized prior to disposal for landfill, or burned for destruction/elimination.

Each industry faces its own unique issues when it comes to plating on plastic. Materials used in the current process for aerospace, defense, and space face issues with off-gassing. Other industries like medical devices, automotive, and other high-tech industries encounter issues because many alternative coatings do not provide the level of corrosion resistance as coatings containing cadmium or nickel.

Alliance Finishing's chemistry does not use traditional chemistries to achieve metallization. This technology eliminates the need to remove toxic chemicals from waste streams and results in safer working conditions and safer products for the consumer.



## *Partially Hydrogenated $\beta$ -Farnesene: A Renewable, Pure Hydrocarbon Non-VOC Solvent Produced from Plant Sugars*

Using a state-of-the-art organism engineering platform, Amyris has re-engineered ethanol-producing baker's yeast to consume sugars and convert them into a hydrocarbon rather than an alcohol. Amyris has also demonstrated industrial-scale production of this hydrocarbon using its proprietary yeast strains in a commercial fermentation process, converting any fermentable sugar, including those derived from cellulosic biomass, into *E*-7,11-dimethyl-3-methylene-1,6,10-dodecatriene ( $\beta$ -farnesene, Biofene®). This technology platform can be used to not only produce the 2014 Presidential Green Chemistry Challenge Award winning drop-in diesel and jet fuel blendstock 2,6,10-trimethyldodecane, but it also provides an innovative renewable building block molecule applicable in numerous industrial areas, ranging from novel polymers with unique properties to value-added cosmetic and fragrance ingredients. In keeping with the Amyris mission to address daunting global challenges, the company has now used  $\beta$ -farnesene to manufacture partially hydrogenated farnesene on an industrial scale by a simple, efficient, and economical catalytic hydrogenation, thus bringing to market a unique organic solvent that addresses the environmental, health, and performance issues of existing solvents, both renewable and petroleum-based. With its regulatory approval in the U.S. and E.U. in 2015, the commercial launch of this newly designed chemical is expected to have a significant impact in the solvent marketplace, where human exposure, health and environmental impacts, and biodegradability continue to be significant concerns.

## **Biosynthetic Technologies**

## *Estolides: A Low-Cost, High-Performance Renewable Fluid Certified for Motor Oil*

This new chemical boasts superior performance as a base oil (the majority fluid) in motor oil and other industrial lubricant applications. This class of clean lubricant base oils, known as estolides, are synthesized from fatty acids found in soybeans and other crop sources through a proprietary catalytic process.

As a vegetable-based specialty fluid, estolides reduce negative impacts on the environment by displacing the petroleum-derived oils dominating the lubricants market today. Automotive and industrial lubricants carry a staggering pollution profile. While renewable fuels, clean energy, and other technologies are advancing to displace their respective incumbent technologies, no viable solution has emerged in the motor oil sector. Enormous pollution from motor oil continuously harms U.S. waterways. With the introduction of the highly stable estolide compound, lubricant manufacturers finally have a base oil option that functions impressively across the many severe applications in which lubricants are used. Estolides conquered the most daunting of these—motor oil—in 2014.

Significant displacement of toxic petrochemicals will occur as estolides are adopted in the industrial lubricant industry. Biosynthetic Technologies has entered into commercialization partnerships with Valvoline, Infineum (a joint venture between ExxonMobil and Shell), Castrol, and other major lubricant brands to help bring this technology to market. These companies have formulated and intend to launch finished products blended with a significant concentration of Biosynthetic Technologies' renewable estolide base oil.

In addition to reduced water pollution, estolides are biodegradable and emit less greenhouse gases across their lifecycle. A third-party lifecycle analysis has confirmed that the emissions associated with estolides are significantly lower than that of comparably performing, petrochemical base oils.



With landmark American Petroleum Institute motor oil certification in hand, an operating demonstration plant, and a commercial plant on the verge of breaking ground, this technology is poised to disrupt the petrochemical-dominant industrial lubricant sector and significantly reduce the environmental harm caused by such oils

## *Disruptive Methanotropic Technology for Sustainable Food, Fuel and Products: Green Chemistry Innovation Enabling U.S. Global Competitiveness in Low-Carbon, New Economy*

**Calysta**

Calysta creates high value industrial and consumer products by converting methane into sustainable building blocks for life, while reducing source pollution. Calysta has developed and is deploying a proprietary genetic engineering platform for host organisms (methanotrophs) capable of metabolizing methane to biofuels, biochemical, and bioproducts, such as Feedkind aquaculture protein. The genetic tools, together with innovative fermentation and bioprocess approaches, enable the rapid implementation of well-characterized pathways to use natural gas and biobased methane as a biological feedstock instead of sugar. Methane's global warming potential (GWP) is 30-times greater than that of CO<sub>2</sub>, implying that capturing these sources will have a significant environmental benefit. Longer term, biomass-to-methane strategies may enable a fully renewable carbon cycle if "green" methane-based technologies are developed.

## *Catalytic Electrolysis for Renewable Fuel Generation from Organic Waste Water*

**Catalytic  
Innovations, LLC**

Organic-containing wastewater from manufacturing in the dairy, pharmaceutical, cosmetic, dye, adhesive, pesticide, and other industries are extremely high volume, hazardous to the environment, and energy-intensive to remediate. In many cases, they possess low pH, further complicating their treatment. Current state-of-the-art technologies to treat organic wastewater use multi-step treatment that includes bio-digestion stages that are unstable, energy-intensive, and costly. This technology offers an alternative method for organic wastewater treatment using selective catalytic electrolysis. Using recently discovered surface-bound molecular electrocatalysts, which possess the stability of heterogeneous oxides and the selectivity of homogeneous molecular complexes, Catalytic Innovations is able to selectively oxidize harmful organic compounds to CO<sub>2</sub> in aqueous environments. When integrated into a bipolar polymer electrolyte membrane electrolyzer stack, a concentrated stream of CO<sub>2</sub> is produced at the anode with concomitant production of H<sub>2</sub> via proton reduction at the cathode, while clean, organic-free water with a near-neutral pH is discharged. The water can be safely discharged or re-used in the manufacturing process. Due to their concentrated output streams, the resulting H<sub>2</sub> can be used as a carbon-free renewable fuel, while the CO<sub>2</sub> is liquefied and sold as a commodity. Proof-of-concept experiments for these reactions have been completed, and functioning lab-scale electrolyzer stacks are in use for both dairy and pharmaceutical wastewater. Development of a pilot reactor and plant for the dairy industry is currently underway. The pilot plant alone will prevent 25,000 gallons per day of hazardous waste water from negatively impacting the environment, and if successful, the first generation of these electrochemical reactors would displace 15 million gallons per day of aqueous hazardous waste in the U.S. alone. Across all industries and worldwide, this number increases drastically as this technology has the potential to tackle the global problem of organic wastewater.

## *PeroxyMAX™ Oxidant Technology for Pollution Prevention in Industrial Sectors*

Clean Chemistry has introduced a new advanced oxidation chemical technology, PeroxyMAX™, to the marketplace, creating new opportunities to achieve greater efficiency, safety, water reuse, and pollution prevention in industrial sectors that are historically the largest sources of pollution including energy, pulp and paper, mining, textiles, and manufacturing. The most common industrial oxidants and disinfectants produce toxic residuals, are highly corrosive, or underperform. Some are shelf-stable liquids (and solids) with modest activity while others are highly toxic gases that are hazardous to produce, handle, and store. The PeroxyMAX™ oxidant activity lies between these extremes as a liquid formulation with high activity and selectivity provided by a mixture of reactive oxygen species (ROS) not available previously in bulk quantities. This new source of ROS provides high performance in industrial applications while being safer and less polluting than ozone, chlorine, or chlorine dioxide gases. PeroxyMAX's performance and pollution prevention benefits are greatest in highly contaminated environments where other oxidation chemistries lose efficiency, damage equipment, produce toxic byproducts, and persist in the environment. PeroxyMAX™ avoids the formation of bromate in seawater, groundwater, and wastewater and dramatically reduces organic halide formation in pulp bleaching. The oxidant is relatively short-lived, leaving behind non-toxic, readily biodegradable residuals. The PeroxyMAX™ technology has been deployed at full scale in the oil and gas sector and is now gaining attention in the pulp and paper and natural fiber industries as a safer, less polluting, less corrosive, and better performing alternative to chlorine chemistries. The high performance of PeroxyMAX™ allows it to compete aggressively with the direct cost of conventional industrial oxidants while reducing pollution and increasing safety.

## *Delta S™: An Environmentally Benign and Worker Safe Asphalt Rejuvenator*

Delta S™ is a green chemistry technology that rejuvenates recycled asphalt pavement (RAP) and recycled asphalt shingles (RAS) in asphalt mix designs. Currently, many additives used in asphalt rejuvenation are petroleum-based and pose environmental and worker safety hazards. Delta S™, developed at the Warner Babcock Institute for Green Chemistry by Collaborative Aggregates, is an environmentally friendly, biobased product comprising a small molecule dispersion in a carrier oil. This product is cost-competitive and has been proven to perform as well as, if not better than, currently available asphalt additives. Incorporation of Delta S™ in asphalt mix designs has been shown to increase the acceptable amount of recycled material from 15% to greater than 60%. Implementation of recycled materials at these levels has the potential to reduce virgin material consumption in new mix designs in the U.S. by more than 200 million tons annually. Delta S™ has a number of additional functions: it is a warm mix additive (lowers mixing temperatures); compaction aid; binder modifier (changes performance grade of liquid asphalt); and anti-strip (increases bond strength between liquid asphalt and aggregate). Milestones recently achieved include starting full-scale production, full patent acceptance, and paving on the National Center for Asphalt Technology test track using a high RAP and RAS mix design. This application is supported by extensive third-party laboratory testing along with many large-scale, field trials in a range of climatic conditions.

## *Membrane Dehydration for Solvent Recovery and Reuse*

While solvents are valuable processing tools in the chemical and other industries, the environmental impacts from solvents used as manufacturing and processing aids could be significantly reduced if the product life of solvents were extended beyond single use.

The Compact Membrane Systems technology can effectively reduce the amount of solvent produced, consumed, and entering waste streams in the U.S., by effectively enabling solvent users to recycle and reuse their solvent on site rather than buying large quantities of new solvent and sending that same spent solvent downstream a short time later. Currently, dehydration of solvents to high levels of purity and low levels of water is a major economic and technological challenge, resulting in spent solvent heading downstream to incineration rather than being reused.

Compact Membrane Systems has developed a novel modular membrane-based technology that can dry a broad range of solvents to anhydrous levels, enabling solvent recycling in a broad range of applications where no recycling alternative previously existed. For the first time, solvents can be cost effectively dried to the level of virgin materials and reused onsite rather than disposed. The Compact Membrane Systems technology works effectively with many commonly used solvents of all types, including isopropyl and other alcohols as well as solvents with large release volumes, such as methyl ethyl ketone, tetrahydrofuran, butanol, ethanol, toluene, xylene, and ionic liquids. Many of the solvents of interest to EPA form mixtures with water that are difficult and/or energy-intensive to separate with conventional separation technologies such as distillation. An energy-efficient, cost-effective, and non-polluting alternative technology like that developed by Compact Membrane Systems makes solvent recycling more feasible and economically attractive, ultimately reducing source production of solvents.

## *Mg-Rich Primer for Chrome-Free Protection of Aluminum and its Alloys*

The magnesium (Mg)-rich primer was invented, developed, formulated, and scaled up commercially to create a protective material for aluminum alloys that is free of carcinogenic hexavalent chromium (CrVI).

CrVI is a very effective corrosion inhibitor for aluminum and its alloys, but it is a known carcinogen and is banned from many commercial applications. The U.S. Occupational Safety and Health Administration has reduced the allowable use in the aerospace field and there are efforts to eliminate its use within the U.S. Department of Defense. The Mg-rich primer was initially developed using grants from the U.S. Air Force at North Dakota State University and commercialized by AkzoNobel Aerospace Coatings and Elinor in the civil and military markets. It is currently qualified for use by the U.S. Air Force and there are efforts underway to qualify it for use by the U.S. Navy and U.S. Army.

The primer is based on the concept of sacrificial protection, when two metals are in contact and exposed to a corrosive environment, the more active reacts preferentially and protects the other metal. Magnesium is more active than aluminum and when they are in contact, aluminum is protected from corrosion.

The technology uses granulated Mg as a pigment and blended with solvents and polymers in a primer formulation to develop a sacrificial coating. Many polymeric binders and solvents were tested to reach the optimized formula that affords long-term, carcinogen-free protection to aluminum alloys, very common material for the construction of airplanes, ground vehicles, and marine vessels both for the military and for civil aviation.

The primer was extensively tested in the laboratory, weathered outside in several locations in the U.S., and outperformed the commercially-available chromated primers. It was successfully scaled up to commercial quantities and it is currently available commercially through AkzoNobel Aerospace Coatings and Elinor.

**Compact Membrane  
Systems, Inc.**

**Elinor Specialty  
Coatings; Professor  
Gordon Bierwagen,  
North Dakota State  
University;  
AkzoNobel  
Aerospace Coatings**

## *Floral Soil™: A Green Chemistry Alternative to Phenol Formaldehyde Foams for Floral & Horticulture Industries*

Floral Soil, LLC is a specialty floral supplier based in Bellingham, WA with a small manufacturing operation located in Everett, WA. Floral Soil™ has the potential to disrupt a global market for synthetic floral foams worth hundreds of millions of dollars. Synthetic floral foams are made from phenol formaldehyde resins. Floral Soil™ was conceived by CEO and owner Mickey Blake in her kitchen as a replacement for synthetic floral foams. First introduced to the floral and horticulture industry in 1954, the market for floral foams is now global and worth hundreds of millions of dollars. By modern values, however, floral foams are an unnecessary risk to health and environment.

Floral Soil™ is a 100% biobased, non-toxic, sustainably-sourced, resin and fiber composite useful for a variety of artistic, floral, and horticultural applications. Floral Soil™ is primarily used as a structural medium for displaying cut flowers, while providing water and nutrients to keep them fresh and vibrant. Flower delivery services also use it as a transport container. Unlike floral foams, which persist for decades, Floral Soil™ can be re-used as a growth medium for new plants. Floral Soil™ was designed for the next life and for future generations.

## *Cooling Tower Water Conservation & Chemical Treatment Elimination*

Properly engineered electrolytic extraction of calcium carbonate from recirculating cooling water has successfully controlled deposit formation on heat exchange and other surfaces in practical systems such as industrial and HVAC cooling tower systems. Electrolysis of ionic-rich water produces exploitable *in situ* chemistry requiring no external chemical reagent other than electricity. A *Green Machine* consists of a series of steel tubes that are made the cathodic element of an electrolytic cell where water is reduced to form molecular hydrogen and hydroxide ion, and calcium carbonate is subsequently made to accumulate. Centered in each tube typically is a titanium rod coated with a mixture of ruthenium and iridium oxides, and made the anode of the electrolytic cell. The common name for an anode of this type is “dimensionally stable anode”, or DSA. It is the coating of the anode that is critical in driving the oxidation of water to produce molecular oxygen, hydrogen ion and higher oxygen species such as hydroxyl free radicals and ozone. DSA technology allows for the efficient splitting of water at a low practical voltage potential above that theoretically required, the difference being termed “overpotential.” DSAs have been responsible for past Green Machine success. Supplementing DSA’s with anodes coated with boron-doped, ultrananocrystalline diamond now allows control over troublesome calcium carbonate deposition as well as more efficient *in situ* chlorine formation and degradation of organic contaminants. Microbiological control in cooling water is significantly more efficient.

## *Evolution Polymerization to Produce Sustainable Polycarbonate Dendrimers*

This technology demonstrates the cost-effective and environmentally safe production of sustainable aliphatic polycarbonate dendrimers, a type of nanotechnology, for replacing the 7,000,000 tons of unsustainable polyol produced in the world today for the coatings, adhesives, and sealants (CASE) markets. Dendrimers are spherical shaped polymers that branch out from a central core, like a molecular cell, with a specific core and surface. A proprietary biomimetic process that Instrumental Polymer Technologies, LLC calls “evolution polymerization” is used to make these dendrimers, trademarked QUICKSTAR™, at a price competitive to current polyols.

The unique shape of these dendrimers are being used to minimize the broader environmental impact of the CASE markets by reducing the volatile organic components (VOCs) of coatings, improving the performance of water-based coatings, using less energy during manufacturing of polymers, coatings and finished goods, as well as eliminating the use of toxic and unsustainable epoxies, isocyanates, and aziridine. The unique chemistry and shape of these dendrimers also have environmental benefits outside the CASE markets. For example, they are being used to improve the performance of organic lubricants, and make low density foam more practical. They are even being used as a thermosetting thermoplastic, which can ultimately offer a sustainable, and better performing alternative to unsustainable polycarbonate thermoplastic. The QUICKSTAR™ product line, launched in 2013, reached sales of \$130,000 during 2015 and is climbing quickly in these different markets.

From the broadest aspect, this technology demonstrates the use of a natural growth process, in which molecules undergo a dynamic process of free interaction in a cyclic pattern of growth and fragmentation to yield a polymeric structure of increasing specific complexity. This is in contrast to the step-by-step reactions of classic chemistry which become very expensive, for complex molecules.

## *SPLAT® VERB: An Insecticide-Free, Green Repellent for Bark Beetle Pests of North American Forestry*

The mountain pine beetle (MPB) is one of the most destructive pests of U.S. forests, causing billions of dollars in losses annually. Recent outbreaks of MPB-related tree mortality have occurred on an unprecedented scale, and are show no signs of slowing. Warming trends caused by climate change and shifts in forest structure may favor its spread to even greater areas. Few chemical options are available to control MPB, limited to drenches of the entire tree using large amounts of conventional insecticides, which are environmentally unsound, and impractical to implement on a large scale. SPLAT® Verb is a novel management platform that effectively protects individual trees and pine stands against MPB, without the need for chemical toxicants. SPLAT® Verb relies instead on a natural repellent semiochemical: MPB's own anti-aggregation pheromone, verbenone, a non-toxic compound approved by FDA as a food additive, presenting no risk of harm to non-targets. SPLAT® Verb provides continuous release of verbenone for 3-6 months at levels that fully disrupt MPB mass-attack behavior, something no other verbenone-based repellent has ever been able to achieve consistently under field conditions. SPLAT® Verb was released commercially in 2014, and has since protected hundreds of thousands of trees from MPB, preventing application of more than 60,000 pounds of formulated toxic carbamate insecticides to national forests, city parks, and backyards. This impact is expected to expand as SPLAT® Verb continues to penetrate the market, and as mechanized application becomes feasible on larger scales. Aerial application of SPLAT® Verb could protect entire tracts of forest, stopping MPB expansion, reducing tree mortality and associated forest fires, and virtually eliminating the use of conventional pesticide to manage this pest.

## *Carbon Engineering Platform*

Kiverdi is currently commercializing replacements for specialty oils and oleochemicals derived from CO<sub>2</sub> and/or carbon monoxide (CO) using a proprietary Carbon Engineering Platform, which consists of proprietary knallgas bio-catalysts and a gas bio-conversion process. Kiverdi's technology converts CO<sub>2</sub>, CO, and/or gasified biomass into a diverse range of high value, renewable oleochemical and specialty oil intermediates, which are the building blocks for everyday products such as surfactants, polymers, cleaners, personal care products, and lubricants.

**ISCA Technologies,  
Inc.**

**Kiverdi**



Kiverdi's technology competes on cost and performance. Instead of building larger plants to drive economies of scale, Kiverdi's solution fills a "scale gap" to optimize supply chain costs using local, low capital plants. The combination of low-cost, flexible feedstock and high-yield CO<sub>2</sub>/CO bioprocessing enables Kiverdi to produce Carbon Engineered Products with low capital and materials costs, driving higher margins and superior cost competitiveness. Kiverdi can customize molecules specific to its customers' process and business needs, improving performance and achieving sustainability goals.

Kiverdi has secured a commercialization partner and is now in the process of industrializing its first product line, PALM+, which can serve as a sustainable replacement to palm oil. Kiverdi's second product line is underway - a sustainable, nontoxic, biodegradable cleaner.

## Lygos, Inc.

### *Integrated Production of Sustainable Biobased Malonic Acid for Significant Source Pollution Reduction, Cost, and Performance Advantages*

Lygos has developed a biological process to produce malonates (including malonic acid and its derivative diesters, dimethyl malonate, and diethyl malonate) from renewable raw materials, namely sugars derived from corn, or non-food, biomass feedstocks. The process is a low pH yeast fermentation that converts glucose into malonic acid at high yield and rate. The low pH fermentation process requires minimal addition of base and enables a near zero waste process during subsequent purification of malonic acid from the fermentation broth. Following isolation of malonic acid, esterification is used to produce dimethyl or diethyl malonate, articles of commerce sold in addition to malonic acid itself.

The total malonates market is estimated to exceed 50,000 metric tons, all of which are currently produced from chloroacetic acid and sodium cyanide using a synthetic process. Both monochloroacetic acid and sodium cyanide are listed as extremely hazardous substances and their usage presents substantial environmental and health hazards. Replacement of the incumbent petrochemical process with Lygos' biological process eliminates an estimated 48,000 metric tons of monochloroacetic acid and 27,000 metric tons of sodium cyanide from use. Additionally, 100% of the material in malonic acid produced using Lygos' fermentation process is renewably derived and the fermentation process is performed at atmospheric temperatures and pressures, characteristics that reduce the energy intensity relative to the petrochemical process.

At commercial scales, Lygos' biological process can produce malonates at less than the monochloroacetic acid raw material cost in the current process, reducing both the cost and environmental concerns that have restricted market growth to date. If produced at lower cost, malonates offer additional performance benefits, including low toxicity and biodegradability, characteristics important for new polymer, resin, and solvent applications. Additionally, when coupled with existing green chemistry technologies (e.g., Knoevenagel condensation), low-cost malonates enable commercialization of new routes to various specialty chemicals.

## Marrone Bio Innovations

### *GRANDEVO® Advanced Bioinsecticides*

GRANDEVO® is an EPA FIFRA-registered insecticide, miticide, and nematicide. The technical grade active ingredient is a *Chromobacterium subtsugae* bacterium isolated from a soil sample collected beneath a hemlock tree in Maryland by Dr. Phyllis Martin. The current commercial formulation was registered in 2013. Grandevo® offers complex modes of action to manage a broad spectrum of chewing and sucking insects and mites on a wide range of crops. It provides a unique combination of long-lasting performance and operational flexibility. Unlike

certain chemicals that are suspected of harming honeybees, extensive testing of Grandevo® has shown no negative effects to honeybee health, activity, or pollination when applied as directed on the EPA-approved label. Toxicity testing has shown that Grandevo® presents low risk to key beneficial insects and is not harmful to earthworms. The product is readily biodegradable and is exempt from residue tolerances. Similarly, its lack of toxicity to humans is of benefit to farmworker safety. Grandevo® has minimal farmworker reentry interval and pre-harvest interval requirements. Crops can be harvested on the same day they are sprayed with Grandevo®.

Grandevo® serves growers as an effective and reliable insecticide/miticide that is highly compatible with both integrated pest management (IPM) and insect resistance management (IRM) programs. Naturally-derived from a newly discovered bacterium, Grandevo® is powered by multiple compounds with highly-effective insecticidal properties, giving rise to complex modes of action. These natural compounds are produced by bacterial cells during the manufacturing fermentation process. The result is a potent biopesticide that controls insects and mites via ingestion and repellency. When ingested, Grandevo® controls pests through novel combinations of reduced feeding, oviposition, and fecundity (i.e., ability of the pest to reproduce). Grandevo is paving the way for new, innovative uses of advanced microbial insecticides in modern field and greenhouse pest management programs while providing many human and environmental safety benefits. Used alone or in combination with other pesticides, Grandevo® offers exceptional control of labeled pests along with operational flexibility—making it ideal for use as the foundation or platform component for highly effective IPM and IRM programs for both conventional and organic growers.

## ZEQUANOX®

ZEQUANOX® is the industry's only selective and environmentally compatible molluscicide for the control of invasive zebra and quagga mussels (*Dreissena* species) at all stages of maturity—from veliger (larvae) to adult. ZEQUANOX® is EPA-approved for both in-pipe and open water treatments. It delivers efficacy comparable to chemical solutions such as chlorine, quaternary ammonium, potash, and copper, but unlike these compounds, does not endanger employees, damage equipment, or result in harmful impacts to the environment or other aquatic organisms when used as directed. Composed of dead microbial cells, ZEQUANOX® is classified as a reduced-risk aquatic pesticide with minimal restrictions on usage (e.g., time of year, etc.) and carries only minimal permitting requirements. The product can be applied using standard injection equipment and applicators need only minimal personal protective equipment. While traditional chemical applications typically require lengthy exposure times, ZEQUANOX® treatments can occur over a brief two to eight hour period (depending on treatment goals), within business hours of one workday without disrupting normal operations. The product is noncorrosive to equipment and does not require detoxification before being discharged into receiving water bodies. Unlike mechanical solutions, ZEQUANOX® can be employed quickly, without making a significant capital investment or undertaking a complicated installation. ZEQUANOX® also does not require on-going equipment maintenance to ensure efficacy. Applied directly into the water system like other water treatment products, ZEQUANOX® offers the added benefit of being able to reach and treat even the smallest of crevices where mussels may colonize. With ZEQUANOX®, facility operators are armed with an effective, non-disruptive, and simple solution for controlling invasive mussels throughout their facilities.

**Marrone Bio  
Innovations**

## *Degradable Polymers for Fracking Applications*

Each year, thousands of wells are hydraulically fracked around the world utilizing millions of gallons of water per well. The water is treated with many chemicals, a process that has raised concerns about underground pollution through seepage and the disposal of water after use. Current methods deploy natural thickeners such as guar gum. The thickeners must in many instances be treated after the well is fracked, causing increased water usage and putting a strain on the production of the guar gum, which is grown mainly in India.

Steve Wann and his group of scientists at Meridian Holdings Group specialize in the creation of compostable and biodegradable polymers that help address environmental issues. Seeing the need for a better solution to the fracking process, Meridian Holdings Group scientists designed a broad range of degradable fracking polymers based upon downhole temperatures. The polymers form viscous gels at a defined viscosity and carry proppant under pressure in fracking operations.

The polymers are designed to degrade in days to weeks depending on the requirements of the downhole geology. This property results in little to no post-completion cleanup of the well. Because these polymers break down into biodegradable acids, such as lactic and glycolic acid, the potential for underground pollution through seepage is reduced. The need for safe disposal of water used in the process is also reduced.

Meridian Holdings Group's degradable fracking polymers mitigate the environmental impact of hydraulic fracking by reducing water, energy, and chemical usage during the fracking process. On a broader level, the impact of the degradable fracking polymers are threefold: (1) the polymers displace environmentally damaging substances used for the same purpose; (2) the polymers organically decompose after disposal without industrial assistance, leaving no toxic trace; and (3) use of the polymers reduces water usage and related transportation costs.

## *Renewable Oils for High Performance Lubricants*

Novvi has developed, industrialized, and applied a combination of 21<sup>st</sup> century advances in synthetic biology with traditional petrochemical. Green chemistry can only succeed if it can beat the price and performance of the fossil fuel alternatives and Novvi has provided a product to do this in a significant market that can have a major impact on the environment. Five years ago, there were no viable alternatives to fossil fuel-derived oils that could meet automotive original equipment manufacturer standards. Novvi accepted this challenge and designed high performance hydrocarbon oils from plant sugars that are analogues for the highest performing petroleum products. Novvi's oils reduce carbon emissions in production and use, improve fuel economy in automobiles, and reduce the hazards to the environment during use from its biodegradability characteristics that can only come from synthetic biology.

Today, 98% of oils and lubricants are petroleum-based hydrocarbon molecules, despite an increasing call for alternatives. Many technologies have tried and failed to meet this need, mainly oleochemicals from vegetable oils, because they cannot provide the performance necessary. Novvi recognized the criterion for disrupting the market and designed its oils to reduce environmental impact while competing on performance and cost in order to replace petroleum in a broad and meaningful way. Novvi is the first to commercially produce renewable oils that offer superior performance and biodegradability at a competitive price. This is a significant industry achievement that will drive immense environmental benefit across the \$123 billion lubricant market.



## *Bio-Derived Oligomer Technology to Replace Bis Phenol-A (BPA)-Based Thermoset Coatings: A Practical Solution for BPA-Free Metal Can Coatings for Beer, Beverage, and Food Containers*

Every year, over 0.4 million metric tons of fossil-based BPA-containing epoxy coatings are produced in the U.S. The Ohio Soybean Council, Battelle, and Redwood Innovation Partners, LLC teamed up to develop and market a practical, ready-to-implement, and safe bio-derived solution to replace current BPA coatings. The currently targeted applications are beer, beverage, and food can containers. Battelle performed the initial research for this technology with funding support from the Ohio Soybean Council. The joint effort has resulted in a cost-competitive, highly marketable product that has no known health concerns and is compatible with current industry practice; thus it can serve as a drop-in replacement for BPA-containing epoxy resins in metal can coatings. The first product is Soy-PK resin and development is underway for more such products such as reactive oligomers derived from renewable resources such as plant triglyceride oils. Production using the replacement coatings has been scaled up successfully, and the resulting products have been offered to several U.S. and European coating manufacturers for evaluation. Laboratory testing and preliminary feedback from the field show the reactive oligomer product, Soy-PK resin, has properties and performance comparable to current BPA-based can coatings. Preliminary techno-economic analysis indicates that the reactive oligomer is competitive with current BPA-based epoxy resins at less than \$1 per pound in large commercial scale.

**Rennovia Inc.**

## *Breakthrough Catalyst Technology Enables Cost Competitive Drop-in Bio-Based Nylons and Polyurethanes*

Rennovia has developed new catalysts and processes for the cost competitive production of biobased adipic acid, 1,6-hexanediol (1,6-HDO), and hexamethylenediamine (HMD) from sugars. Lifecycle assessments indicate major reductions in carbon footprint versus traditional petrochemical derived products. Combining Rennovia's adipic acid and HMD enables the production of 100% biobased nylon-66.

Combining Rennovia's adipic acid and 1,6-HDO enables production of 100% biobased aliphatic polyester polyols. Rennovia's biobased HMD can be converted to hexamethylene diisocyanate with at least 75% biobased carbon content, which when combined with 100% biobased aliphatic polyester polyols allows production of aliphatic polyurethanes with very high (>95%) biobased content.

All of these key intermediates are designed to be "drop-in" replacements for traditional petrochemical derived products, enabling for the first time commercialization of more sustainable mainstream nylon and polyurethane polymers without compromising performance or cost.

Following successful lab demonstration of these processes, Rennovia and its partners are completing the engineering design packages for commercial scale (>100 kTA) manufacturing plants via construction and operation of mini-plants.

## *Converting Landfill Wastes to Multi-Functional Green Polyols for Coating Applications*

Environmental, health and safety concerns continue to drive rapid growth for environmentally friendly, low VOC coatings. This growth, further compounded by increased social awareness of mega trends – including depleting finite resources, the growing world population, and constrained food resource – has companies seeking highly sustainable feedstock solutions. Although biobased materials have provided feedstock options, which are more sustainable than fossil petroleum alternatives, use of recycled content has remained relatively unexplored. With this in mind, Resinate Materials Group® has developed proprietary technology, which allows the creation of multi-functional coatings using recycled and biobased raw material streams, including recycled poly(ethylene terephthalate) (rPET), recycled aircraft deicing fluids (propylene glycol), recycled polycarbonate, post-industrial recycled diethylene glycol, biobased dimer fatty acids, and biobased succinic acid among others. By harvesting spent materials otherwise destined for landfills, Resinate scientists have been able to extend the lifecycle of valuable, finite resources. Furthermore, studies have shown recycled PET to have more favorable lifecycle assessment scores than comparable fossil petroleum-based or biobased PET materials. By harnessing the inherent properties of recycled PET, Resinate scientists have been able to impart a unique balance of properties into a variety of functional polyols and coatings, including excellent hardness, good flexibility, corrosion resistance as well as good chemical and stain resistance. Most of these high performance polyols are greater than 90% green, as defined by their recycle and biobased contents.

## *Rivertop Renewables - Sugar Oxidation Process*

Rivertop Renewables has developed an elegantly simple commercial-scale oxidation technology for converting renewable plant sugars into high performing, cost-effective sugar acid products. The process, designed to minimize waste and maximize product yield, is not only economically viable but also inherently green. Rivertop's first commercial production facility (10 million pound/year capacity) completed construction and began testing operations in August 2015. The process was scaled rapidly and at a surprisingly low capital cost.

Rivertop's platform oxidation technology is now being harnessed for the world's first large-scale production of glucaric acid and glucarate salts. Rivertop is now producing and marketing its first glucarate-based products: *Riose*® detergent builder, a high-performing, biodegradable chelator for use in consumer detergents; *Headwaters*® corrosion inhibitor, which is added to salt brines used to de-ice roads; and *Waterline*™ corrosion inhibitors and descalers for use in water treatment markets where replacement of phosphorus and other environmentally undesirable ingredients is an ongoing challenge.

Rivertop's patented process reduces greenhouse gas emissions and land requirements by using every carbon atom of renewable sugar feedstocks. One of Rivertop's first products (*Riose*®) is an alternative to billions of pounds of phosphates found in detergents that pollute waterways around the world. Compared to open reactor oxidation processes, the company's first closed reactor production facility can prevent the release of 5-12 tons of nitrogen dioxide. When used as corrosion inhibitors, glucarate salts (*Headwaters*®) can reduce metal corrosion by 70%, keeping vehicles, roads, bridges and other infrastructure safer and maintenance budgets smaller.

Beyond glucaric acid, Rivertop's process offers sustainable production options for a variety of valuable sugar acids, including xylaric, glyceric, mannaric, and corresponding acids of starch and cellulose. Although Rivertop is at an early stage in market development, the potential economic and environmental impact of Rivertop's oxidation process has attracted a growing group of brand owners and investors.

## *Input and Waste Associated with the Isomerization of Linear Alpha Olefins*

ActiveIsom<sup>®</sup> is an alumina-supported sodium oxide catalyst that is used to isomerize olefins for a variety of industrial applications. Its unique combination of basicity, active site concentrations and ease of use provides chemical manufacturers with a greener isomerization pathway compared to homogeneous or heterogeneous catalyst systems used for the same purpose.

As a replacement for either heterogeneous or homogeneous catalysts, ActiveIsom<sup>®</sup> delivers linear alpha olefins that are high purity and offer favorable economics. In 2015, a pilot production trial was completed at Dixie and a new commercial processing unit was designed. The new ActiveIsom<sup>®</sup> processing unit will be implemented at Dixie in 2016, achieving an 85% reduction in the generation of toxic byproducts, significant decrease in energy inputs, and a greater than 80% reduction in manpower requirements. Additional pilot-scale evaluation projects for this catalyst are also underway at global ethylidene norbornene producers.

**SiGNa Chemistry,  
Inc.; Dixie Chemical  
Company, Inc.**

## *Environmental Protection Reagents from MSW: One-Step Quantitative Resourcing Municipal Solid Waste*

Quantitative recycling of municipal solid waste (MSW) is crucial for environmental protection and resources preservation. With a novel catalytic system and special designed reactor, CoDOP (Catalytic One-pot Hydrolytic Depolymerization of All Natural Organic Polymers) MSW resourcing technology quantitatively converts MSW into five products in a one-step reaction with no garbage sorting or drying needed: (1) Product A; (2) Product B; (3) high purity SiO<sub>2</sub>; (4) noble metals; and (5) phosphates and nitrogen chemicals.

High efficacy of Product A in absorbing heavy metals, PHAs, CO, sulfur oxide, and nitrogen oxide make it an ideal substance for economically cleaning industrial waste gases and heavily polluted water. The cost of removing mercury from industrial waste gases is less than 1% of that using ACI (active carbon injection) method. The absorbing ability of Product A for heavy metals from water is similar to that of Diphonix resin. Product B is an ideal scavenger of carbon dioxide and excellent green deicer. The other three products are a mixture of noble metals (e.g., gold, silver, copper, iridium, platinum, etc.), high purity silicon dioxide, and an aqueous solution of nitrogen contained chemicals and phosphates (it can be developed as a fertilizer). For typical MSW of the U.S., the yield of Product A is about 12%, and the yield of Product B is about 70%. The catalytic system catalyzes oxygen atom transfer from aromatic polymers of MSW to carbohydrate components. Neither oxidants nor reductants are used in this one-step reaction. If all MSW collected after recycling and composting is treated with this technology, it will reduce greenhouse gas emissions by about 328 million tons of carbon dioxide per year.

**Sun  
Pharmaceuticals,  
Inc.**

## *SPEAR<sup>™</sup> Insecticide: First Member of a New Class of Biopesticides which Shows Efficacy Comparable to Synthetic Insecticides*

SPEAR<sup>™</sup> is a product whose technology is inspired by the most prodigious predator of insects—spiders. Spiders express peptides intermediate in size between proteins and small molecules and have enjoyed the beneficial attributes of each to yield insecticides that are both highly effective and environmentally benign. These peptides are more stable than proteins for better fit with existing agronomic practice but readily break down into nutritive amino acids. SPEAR<sup>™</sup> is comprised of an active ingredient that is broadly insecticidal, non-toxic to vertebrates, and is produced by fermentation.

**Vestaron  
Corporation**

The SPEAR™ line of insecticides is the first example of a new chemical class of insecticides, cysteine rich peptides. This class of peptides typically adopts a conserved folding structure shared across multiple genres of insect predators. They exist at the midpoint in molecular size between small synthetic molecules and typical proteins. As such, they are able to incorporate the best properties of each.

Over the past 20 years, there have been fitful attempts to develop insect predator peptides as insecticides. Vestaron has surmounted the three key hurdles that have stymied previous efforts: (1) development of cost efficient manufacturing; (2) formulation for oral availability; and (3) EPA regulatory approval.

SPEAR™ is produced by fermentation and then processed to remove yeast. The resultant broth is concentrated and spray-dried to produce a product relying primarily on renewable feedstocks. SPEAR™ is exempt from a tolerance for residue as a consequence of its proteinaceous composition and benign toxicological profile. SPEAR™ operates by a new mode of action and will immediately address emerging insect resistance to currently marketed synthetic insecticides. As it does so, it will rotate with or displace synthetic insecticides that have less than optimal toxicological and environmental fate attributes.

*Accel 5 RTU, an Accelerated Hydrogen Peroxide® (AHP®)  
based cleaner-disinfectant that provides a sustainable and  
safer choice for infection prevention and control*

Chemical disinfectants are widely used in infection control. Reliance on them is increasing further in preventive strategies because of rampant antibiotic resistance and mounting threats from emerging and re-emerging pathogens. An imperative aspect to preventing the spread of these harmful microorganisms is through disinfection of contaminated surfaces. However, concerns for human and environmental safety resulting from the widespread use of microbicides highlights the need for safer substitutes.

As a technology platform, Accelerated Hydrogen Peroxide® (AHP®) is available globally for use as cleaner-disinfectants, instrument reprocessing disinfectants, hand sanitizer, and certified green cleaners. The *Accel 5 RTU* formulation is the first hospital disinfectant based on hydrogen peroxide to be certified under the Design for the Environment Antimicrobial Pesticide Pilot Project.

Hydrogen peroxide is among the oldest microbicides known, and it is generated naturally in many settings. However, it is relatively unstable and somewhat slow-acting when used on its own. Through the development of the AHP® technology, both of these weaknesses have been addressed. The patented AHP® technology is a synergistic blend of commonly-used ingredients that, when combined with low levels of hydrogen peroxide, dramatically increases its germicidal potency and cleaning performance. AHP® contains only those ingredients listed on the CleanGredients list, which contributes to an unsurpassed health, safety, and environmental profile. The stabilizers, surfactants, and other excipients in the *Accel 5 RTU* formulation have a high safety and biodegradability profile and are free from aquatic toxicants such as nonylphenol ethoxylates or alkylphenyl ethoxylates. Furthermore, its corrosivity has been tamed, thus widening its materials compatibility allowing for widespread use in hospitals, educational settings, office, and governmental buildings.

## *Atom-Efficient Process for Producing Taurine*

Taurine is an ingredient for human nutrition and animal feed with several applications. Annual consumption of taurine amounts to 120 million pounds. Taurine is manufactured exclusively by chemical synthesis from ethylene oxide and monoethanolamine, two related petrochemicals. There are three major problems in the current processes: (1) low atom efficiency at 57.6% and 42.7% for ethylene oxide and monoethanolamine, respectively; (2) unsatisfactory molar yield at 75% and 60% for ethylene oxide and monoethanolamine, respectively; and (3) a difficult and complicated separation process. As a result, a large amount of waste, comprised of residual taurine, organic impurities, inorganic salts is generated in the process. Vitaworks, LLC developed a cyclic process for producing taurine from ethylene oxide, sulfur dioxide, and ammonia. The cyclic process features: (1) the use of sulfur dioxide as an acidifying agent and a starting material; (2) cyclic use of alkali; and (3) a newly discovered reaction of ditaurine and tritaurine with ammonia to yield taurine. This technology produces a valuable compound at a large scale with an atom efficiency of 100% in nearly quantitative yield. By adopting this technology, a total of 545 million pounds of starting materials, byproducts, and waste will be reduced annually from the production process. Vitaworks, LLC also developed an alternate process for producing bio-taurine from ethanol, a biorenewable starting material. The process features near quantitative yield from ethanol to taurine, no waste stream, and cyclic use of alkali. As an added benefit, the process is the most economical among the three processes. Five U.S. patents have been granted and two U.S. patent applications are pending for the portfolio of taurine technologies.



# Entries from Industry and Government

## *Alternative to Sulfur Hexafluoride Enables up to 99% Greenhouse Gas Emission Reduction*

3M

Current society revolves around readily available and reliable electricity. Availability and reliability is dependent upon highly structured and complex energy generation and distribution infrastructure (“the grid”). The grid relies upon complex equipment developed over the past seven decades using sulfur hexafluoride (SF<sub>6</sub>) as a dielectric (insulating) fluid. Over the past three decades, the increase in energy density (voltage and amperage) used in the grid has all but eliminated other dielectric fluids and technologies other than SF<sub>6</sub> in high voltage equipment.

The title paragraph from the 2013 EPA SF<sub>6</sub> Emission Reduction Partnership report (April 2014) summarizes the critical impact of SF<sub>6</sub> on the environment and the need to reduce or eliminate SF<sub>6</sub>. Identification of an alternative to SF<sub>6</sub> requires a demanding and unique combination of performance, safety, and environmental attributes. This balance of properties has been exceedingly difficult to find so SF<sub>6</sub>, the most potent greenhouse known, has continued to be the solution of choice.

3M now offers an alternative to SF<sub>6</sub> that will function in many power generation and distribution applications. Replacing SF<sub>6</sub> would effectively replace a material having an atmospheric lifetime of 3,200 years (GWP = 23,500) with a material that has an atmospheric lifetime of 30 years (GWP = 2,100), thus reducing its GWP contribution in these applications and resulting in significant greenhouse gas emission reductions of up to 99% relative to SF<sub>6</sub>. The alternative’s higher dielectric strength provides similar electric insulation at lower use concentration in an inert gas (e.g., air or CO<sub>2</sub>) and has significantly lower density compared to pure SF<sub>6</sub>. These characteristics, lower GWP, reduced use concentration and lower gas density, combined will reduce the total GWP contribution significantly compared to SF<sub>6</sub>.

## *Green Nanotechnology Product and Processes for Cleaning Up Contaminated Soil and Groundwater*

AECOM

This green chemistry innovation involves the successful development, testing, and application of a new green nanotechnology product for treating contaminated soil and groundwater. The product also has applicability as an activator for water and wastewater treatment. As groundwater quality standards have become more stringent to ensure a sustainable water supply for future generations, technologies developed for groundwater restoration have become more energy intensive, costly, and often use hazardous chemicals that can potentially create greenhouse gases or secondary hazardous conditions. Due to its high reactivity, metal nanoparticles have been shown to be effective for degrading certain contaminants. Generally, metal nanoparticles are synthesized in three ways: (1) physically by crushing larger particles; (2) chemically by precipitation; and (3) through gas condensation. The commercial significance of nanoparticles is limited by the nanoparticle synthesis process, which is generally energy intensive, produces air pollutants during the manufacturing processes or requires toxic chemical solvents, and is costly. This green environmental nanotechnology process enables manufacturing metal nanoparticles at ambient temperature and pressure by using certain plant extracts rich in polyphenols, such as green tea, as a reducing agent, dissolved metal ions, and a plant-based surfactant blend. The basic technology can produce a variety of metal nanoparticles that can be used in a variety of applications including soil and groundwater remediation, water and wastewater treatment, air pollution treatment, medical diagnostic testing, medical materials, targeted drug delivery, catalysis of chemical synthesis reactions, pollution control or monitoring devices, fuel cells, or



electronics. During a recent 2015 application at a contaminated industrial site, the green iron nanoparticles were injected into subsurface and safely and effectively reduced chlorinated and non-chlorinated solvent contamination in soil and groundwater.

### *Discovery, Development and Implementation of New Chemical Technology toward a Novel Commercial Synthesis for the HIV-Attachment Inhibitor, BMS-663068*

BMS-663068 is an investigational, oral, HIV-1 attachment inhibitor and a pro-drug of the active compound BMS-626529, which interferes with attachment of the HIV virus to the cellular CD4 receptor. As a first-in-class compound, BMS-663068 has the potential to significantly impact patients' lives. This important new medication is based on an unusual aromatic heterocycle, a 6-azaindole, and contains a phosphonoxymethyl pro-drug moiety. BMS-663068 is a challenging molecule to prepare, though its complexity is hidden in the disposition of functionality around the azaindole nucleus. An existing synthesis, used to support clinical development, was extremely inefficient and potentially limited the commercial viability of this drug. The synthesis contained high temperature transformations, one being conducted in neat POCl<sub>3</sub>, along with processes that generated hazardous byproducts and leveraged reagents dangerous to human health. An innovative, *de novo*, green synthesis was conceptualized, demonstrated, and developed, which obviated all these issues and represents a commercially viable approach to the drug molecule – ensuring access to this important medication while minimizing environmental impact. During the development of this approach, new chemical technologies were discovered for the selective halogenation of aromatic heterocycles, removal of solubilized metal from process streams, and for the formation of the phosphonoxymethyl prodrug chemotype. These new technologies increased the overall yield of BMS-663038 by over 5 fold and eliminated the use of multiple hazardous reagents, including genotoxic compounds. At potential peak commercial volume, the technology is annually expected to reduce over a million kilograms of hazardous chemicals, eliminate 2.7 million kilograms of total reactants/solvents, reduce yearly water consumption by 7.2 million kilograms (total consumption reduced by ~9.9 million kilograms), reduce greenhouse gas emissions by 24 million kilograms of CO<sub>2</sub> equivalents, and significantly reduce energy use. The chemistry is in the final stages of being validated for commercialization

### *FLUEPAC® Activated Carbon Products for Superior Mercury Control from Flue Gas and Green Re-Use of Coal Combustion Residuals*

The federal Mercury and Air Toxics Standards require electric utilities to limit their emissions of toxic air pollutants (such as mercury) from the burning of coal. Many utilities have turned to ACI to help meet these limits. In practice, powdered activated carbon is injected into the flue gas at coal-fired power plants where it captures gaseous mercury in a safe and solid form that is usually comingled with the fly ash from the coal. Given the wide variety of plant configurations and coal types, some plants were found to be much harder to treat with ACI than others. Furthermore, initial results with early first generation carbon products indicated that the carbon would render the fly ash unsuitable for inclusion in ready-mix cement, a beneficial and green re-use of the ash that also generates revenue for utilities. Designed to address these issues, the FLUEPAC® line of activated carbons has evolved from simple commodity-type products, used to control mercury at waste incinerators, to highly engineered materials that can meet the challenging mercury control needs of the coal-fired electric utility fleet. Now in commercial use at power plants across the U.S., the superior cement compatibility and mercury removal performance of these products enable utilities to control mercury reliably and cost-effectively, while preserving fly ash sales and



avoiding unnecessary landfill disposal. All of this translates to as much as 70% less activated carbon and 80% less bromide salts used, fewer truck deliveries, and the prevention of one metric ton of CO<sub>2</sub> emissions for every ton of fly ash sold to the ready mix cement market. Having hit the milestone of over one million tons of fly ash containing FLUEPAC® products sold for use in cement in 2015 alone, means that over one million metric tons of CO<sub>2</sub> emissions were prevented.

## *Dream Production – CO<sub>2</sub> as a New Building Block for High-Tech Plastics*

The incorporation of CO<sub>2</sub> into a polyol brings three key benefits to a former fully petrochemical industry: (1) it provides a more sustainable model by incorporating a byproduct (CO<sub>2</sub>) as a valuable resource, thereby reducing greenhouse gas emissions; (2) it meets the current requirements for polyol manufacturing and usage in polyurethanes; and (3) it is cost-effective. Covestro has joined forces with academic and industrial partners to use CO<sub>2</sub> as a building block for plastics. In this technology project, CO<sub>2</sub> is incorporated into the molecular chains of polymers with the help of a new catalytic process and partially replaces the ubiquitous petroleum-based raw materials. The resulting technology enables the production of polyols with a CO<sub>2</sub> content of roughly 20%. By reducing the emission of CO<sub>2</sub> and dependence on petroleum, reducing energy use, substituting a less hazardous feed stock, and utilizing a catalytic reaction, this process aligns with several of the principles of green chemistry.

A production line with a capacity of 5,000 metric tons per year is currently being built in Germany and is due to go on stream in 2016. These polyols can find first applications as polyurethanes in flexible foams such as mattresses. A detailed lifecycle analysis of the CO<sub>2</sub>-containing polyol showed that due to substitution of greenhouse gas emission-intensive epoxides such as propylene oxide, the amount of avoided greenhouse gas emissions is higher than the amount of CO<sub>2</sub> used as feedstock. This production of 5,000 tons of PO/CO<sub>2</sub> polyol is estimated to reduce emissions of approximately 2,700 tons of CO<sub>2</sub> compared to the standard process. The commissioning of the pilot-scale facility is an important step in the direction of widespread commercialization of the PO/CO<sub>2</sub>-polyols.

## *Dow Polymeric Flame Retardant*

PolyFR is a butadiene styrene brominated copolymer that serves as a polymeric flame retardant (FR) intended for use in PS insulation foams. PolyFR was developed to meet defined performance criteria, including inherently low toxicity, through key design decisions related to molecular size, molecular architecture, and controlled thermal stability. Developed as a replacement for hexabromocyclododecane (HBCD), which is classified as a PBT (persistent, bioaccumulative, and toxic) material, PolyFR directly aligns with the green chemistry goal of eliminating the use and generation of hazardous substances.

HBCD has been used throughout the PS foam insulation industry as the incumbent flame retardant, effective at very low quantities for delivering required fire safety performance. Despite the conclusion that the use of HBCD in PS foam insulation applications does not pose health risks, global regulatory pressure is driving phase-out of HBCD in all applications.

PolyFR emerged as the result of a multi-year research program focused on developing a non-PBT alternative to HBCD for use as a FR in PS insulation foam. Key design criteria included toxicological profile, foam processing performance, foam fire performance, foam thermal insulation performance, foam mechanical properties, and economic feasibility.

The benefits offered by PolyFR include characterization as a non-PBT material, inherently low toxicity relative to HBCD and other low molecular weight chemistries, and effective FR performance. These benefits were confirmed by EPA in its Design for the Environment report on FR alternatives to HBCD.

**Covestro LLC**

**The Dow Chemical Company**

## The Dow Chemical Company

## Dow Microbial Control

The commercial impact of PolyFR has been significant, as PS foam producers globally are converting out of HBCD and to PolyFR. PolyFR was first produced at the commercial scale in 2012, and production has grown to 22,500 MT in 2015. As HBCD continues to face regulatory and market pressure, it is estimated that PolyFR has potential to replace at least 30,000 metric tons per year of HBCD.

### *SOLDERON™ BP Lead-free Solder Plating Chemistry*

SOLDERON™ BP products eliminate lead in advanced semiconductor packaging applications, such as solder bumping and pillar capping. SOLDERON™ BP tin-silver plating chemistries provide electrical and mechanical connections equivalent to industry-standard lead-based solder.

Bumping is an advanced wafer level process technology where solder “bumps” or “balls” are formed during wafer processing. These bumps, formed before the wafer is diced into individual integrated circuits, will electrically and mechanically connect the die and the substrate together into a single package. Solder bumps are deposited using electroplating, and the process must produce very uniform bumps in both size and composition. Manufacturers use them to join semiconductors together, to a substrate, or directly to a circuit board in flip chip or controlled collapse chip connection (C4) packaging.

Solder is a critical element in electronics and must provide connections that are durable and reliable. Tin-lead is an ideal solder because it is malleable and has a low melting point. Tin is combined with lead to provide greater tensile and shear strength and higher conductivity. This combination resulted in an ideal balance of electrical and thermal conductivity and cost. Regulations limiting lead have been enacted due to its high toxicity, especially when electronics reach end of life and are deposited in landfills or recycled.

Materials suppliers have spent most of a decade searching for a lead-free chemistry to match the reliability of tin-lead solders and tin-silver has emerged as the most viable solution. Technology is what differentiates Dow's SOLDERON™ BP tin-silver – patented additives that provide manufacturers with superior performance and low cost of ownership, which will drive wider adoption of lead-free solders in electronics.

### *KATHON™ 7 TL Antimicrobial for Water Treatment Applications*

With increasing emphasis on reducing water consumption, cooling water systems have become more efficient using less water for their operation. Perfectly sized for small to medium sized cooling towers, KATHON™ 7 TL solid biocide offers a more sustainable and safer product than its liquid counterparts. This innovation is the only solid antimicrobial made with the active ingredients chloromethylisothiazolone/methylisothiazolone (CMIT/MIT) and is designed to replace the manual dosing of liquid biocides. The tablet form, wrapped in a water-soluble bag, eliminates the potential for splashes, leaks, improves user safety and handling, and reduces the possibility of accidental environmental release without the need to dispose the wrapper. KATHON™ 7 TL is a 7% active solid, while traditional liquid products are 1.5% active. Therefore, about five times less weight needs to be shipped to treat the same amount of water. The lower level of transportation involved, contributes to the reduction of cost and greenhouse gas emissions. In addition, CMIT/MIT is effective in controlling biofilm, which improves operating efficiency and energy.

The development of KATHON™ 7 TL represents a significant advancement in sustainable microbial control and nearly a decade of research in the making. Development of this innovative product was extremely challenging as the CMIT/MIT active ingredients are inherently unstable in solid form. Adding a binder to the liquid CMIT/MIT to solidify the formulation proved challenging as many binders did not stabilize the active ingredients. In addition, unlike the liquid form of CMIT/MIT, which utilizes copper salts for stabilization, KATHON™ 7 TL was designed

to be free of heavy metal stabilizers. KATHON™ 7 TL is instead stabilized by a unique binder and its solid form. The water-soluble packaging developed for KATHON™ 7 TL also represents a significant technical accomplishment as most water soluble films are incompatible with the formulated tablet.

## *Creation, Integration, and Engineering of the World's Largest Cellulosic Ethanol BioRefinery Production Platform*

This technology integrates chemistry, biology, and process engineering to develop a commercially viable, scalable technology platform for the production of cellulosic sugar and its conversion to ethanol. The work required the integration of a novel pretreatment process, the development of improved enzymes for hydrolysis, and the genetic engineering of a novel, highly efficient fermentation host. The resultant DuPont integrated process is a novel integrated production platform, with three major technology components, for the production of ethanol at sufficiently high yields and titers to achieve commercially viable economics. To optimize the process it was necessary to consider and innovate all three conversion steps holistically. First, a novel dilute ammonia biomass pretreatment process decouples the carbohydrate polymers from the lignin matrix with minimal formation of compounds which inhibit subsequent fermentation, thus eliminating the need for costly “detoxification” steps which are common in other cellulosic ethanol technologies. Next, an enzymatic hydrolysis step uses a novel suite of high performance enzymes specifically engineered by DuPont to depolymerize and hydrolyze both cellulose and hemicellulose to high titers of fermentable sugars in a single sugar stream. Thirdly, DuPont integrated and optimized the metabolic pathways of a recombinant bacterium, *Zymomonas mobilis*, to simultaneously metabolize both 6-carbon (glucose) and 5-carbon (xylose) sugars to efficiently produce ethanol at high yields and titers from the hydrolysate. This unique integration of three technology components enables a very efficient, “clean” flowsheet with minimal steps, a reduced environmental footprint, and reduced cost and capital versus other known cellulosic ethanol processes. DuPont has achieved commercially viable ethanol yields consistently in its 250,000 gallon per year demonstration facility in Vonore, TN yields of more than 70 gallons per U.S. ton of biomass and ethanol titers in excess of 70 g/L have been demonstrated. Comprehensive “Well-to-Wheel” lifecycle analyses show that this combined process has the potential to achieve more than a 100% reduction in greenhouse gas emissions compared to gasoline, which is substantially better than current grain-based ethanol greenhouse gas performance. The DuPont technology has been demonstrated successfully and the first commercial plant for conversion of corn stover to ethanol is under construction in Nevada, IA.

**DuPont**

## *A Greener Process for the Fragrance Veridian and Development/Implementation of IFF's Green Chemistry Tool*

In conjunction with a dramatic company-wide acceleration in a commitment to sustainability, IFF now has a very strong focus on green chemistry. *Veridian*, an IFF fragrance ingredient, was first introduced in 2008. The original two-step synthesis of this compound was via a batch process Grignard addition followed by an Oppenauer oxidation. As the demand for this product grew, a greener synthesis of Veridian was developed using a flow process and a novel catalytic air oxidation. The new synthesis boasts a significant reduction of waste, more efficient use of resources, use of a renewable resource, greater energy efficiency and improved worker safety, along with several economic benefits. In addition, IFF has developed and implemented a Green Chemistry Assessment Tool tailored to IFF needs. The tool was used for these improvements.

**International  
Flavors &  
Fragrances Inc. (IFF)**

## *The Recovery of Organic Halides from Waste Streams by the Chemical Reaction of Hydrogen and Carbon Dioxide*

Fluorocarbon compounds, including chlorofluorocarbons, hydrochlorofluorocarbons, hydrofluorocarbons, perfluorocarbons, and halons, are used in a wide variety of applications including air-conditioning, refrigeration, medical, fire protection, and solvent uses. They are also widely recognized as ozone depleting substances (ODSs) and/or greenhouse gases. At the end of the life of such applications, the chemical is either destroyed, or worse, vented into the atmosphere. This venting, now prohibited in many countries, has been recognized to contribute to the depletion of the stratospheric ozone layer, and is considered a cause of global warming and climate change.

The most common methods of ODS and greenhouse gas destruction are incineration by thermal oxidizer, rotary kiln, and plasma arc. These methods are costly, create their own waste streams and stack emissions, and yield outputs with little or no economic value. Destruction capacity around the world is limited or in some countries, non-existent.

With increased regulation of older fluorocarbon products with high GWP and with the economic and environmental challenges of existing destruction technologies, there is great need for an alternative approach.

The Midwest Conversion Technology not only deals with unwanted ODSs and greenhouse gases, but also can be applied to the waste streams at fluorocarbon manufacturing plants. The outputs are the manufacturing source chemicals, i.e., 99.999% anhydrous hydrogen fluoride, 99.99% anhydrous hydrogen chloride, plus CO, all ready for new use. The technology is original and the process is safe, clean, inexpensive, energy efficient, waste free, and meets almost all sustainability targets. Pilot plant data and computer modeling has demonstrated that this technology can reduce the cost of rotary kiln and plasma arc destruction by 50-60%.

## *SunCryl HP 114, an Environmentally Friendly Release Coat*

A release coat is added during the manufacture of tape to allow tape to be unwound. This release coat backing can also be used for peel-off labels. Fluorochemicals, silicones, or other solvent-based polymers are commonly used for release coats because they maintain their performance at high temperature and humidity. Tape manufacturers are seeking alternatives to these materials in release coats that do not have negative environmental impacts. OMNOVA has developed the first water-based release coat that is free of formaldehyde, solvents, or VOCs but performs equivalently to current technologies. Release coats have the most significant impact on the environmental impact of the finished paper-based tapes and labels, while the solvents utilized in their manufacture contribute to the carbon footprint of manufacturers and users.

OMNOVA has commercialized a water-based polymer, using a novel monomer prepared via a solvent-free production process. This monomer is dispersed in water with alkylphenol ethoxylate free surfactants and polymerized. The only volatile compound in the resulting polymer latex is water. When applied, the release is comparable to the incumbent products. When applied to paper, the finished product is recyclable.

## *A Green, Energy Efficient, Chemoenzymatic Process to Manufacture Pregabalin*

**Pfizer**

Pregabalin (the active ingredient in the drug Lyrica®) is a compound for the successful treatment of several indications associated with neuropathic pain. The drug is approved in 154 countries around the world including the U.S. Pfizer's new route to pregabalin uses an innovative biocatalytic reaction to remove a classical resolution in the final step. The biocatalytic process eliminates the use of organic solvents in all four reaction steps and operates at a high substrate concentration thus providing dramatic improvements in environmental performance, worker safety and process efficiency. The new biocatalytic process has been successfully implemented in a production facility at a 10 metric ton batch size. Pfizer estimates that the new process will eliminate 185,000 metric tons of solvent, 4,800 metric tons of mandelic acid, 11,000 metric tons of the starting cyanodiester, and 2,000 metric tons of Raney® nickel in the years before 2020. The biocatalytic process also uses 83% less energy than the classical resolution process and the E factor of the process has been reduced from 86 to 9.

Pfizer has implemented exceptional green chemistry innovation by using a biocatalytic reaction, conducting reactions in water rather than organic solvents, selectively synthesizing chirality earlier in the process sequence, recycling the undesired enantiomer using a continuous process, telescoping reactions for higher efficiency, and implementing catalytic as opposed to stoichiometric reactions. These improvements result in a biocatalytic process that is more sustainable than the chemical process it replaced. Key innovations were: (1) overcoming product inhibition in the biocatalytic step to allow exceptionally high substrate concentrations; and (2) designing, building and validating a new continuous plant to allow the recycle of the wrong enantiomer.

Pfizer has published the chemistry in a peer-reviewed scientific journal and made the methodology available to the wide scientific community. Finally, pregabalin is one of the very few small molecule pharmaceutical agents where every chemical step in the manufacturing process is performed in water.

## *Cold-Water Enzyme: Reducing the Environmental Footprint of Residential Laundry through Low Temperature Cleaning*

**The Procter & Gamble Company;  
DuPont Company**

Each day, Americans do 123 million loads of laundry. They have become accustomed to a certain level of cleaning and ease in performing this essential activity of modern living. And when it comes to stain removal, most choose to set their dials to warm or hot to ensure a quality clean. The research teams at DuPont and its strategic partner Procter & Gamble have invented an entirely new enzyme that allows consumers to wash their clothes at significantly lower temperatures with dramatically improved performance. The enzyme helps reduce energy use by 50% with each load.

This superior enzyme technology, cold-water protease, is available now in *Tide Coldwater Clean*. Both companies felt passionate about pursuing the development of this enzyme because success meant significant environmental benefits due to the sheer scale of use. Current laundry washing creates 40 million metric tons of emissions of carbon dioxide. If the loads were cleaned instead in cold water, the energy savings would reduce those emissions by 80%. In other words, that is the equivalent of taking 6.3 million cars from the road, based on annual U.S. emissions. Use of this cold-water protease has equivalent performance and stability compared to the traditional technology used. DuPont's Genencor scientists applied novel protein engineering methods to invent an optimal protease enzyme that at 60°F matches the cleaning performance of the previous incumbent generation product at 90°F. Joint commercialization of this breakthrough technology



**Jesse Sabatini, U.S.  
Army Research  
Laboratory**

means it has the potential to become the largest manufacture of an engineered enzyme in the world – greening one of the most common household chores on a macro scale. Consumer habit surveys indicate that low temperature cleaning is on the rise in both North America and Europe, and that the potential benefits enabled by this technology are becoming a reality. In 2015 DuPont and Proctor & Gamble took sustainable innovation one step further by introducing renewable, cellulosic ethanol made from waste agricultural biomass residue into Tide® Coldwater laundry detergent.

### *Environmentally Friendly Colored Pyrotechnic Illuminants*

While perchlorates are ubiquitous in colored pyrotechnic illuminants, they are contaminants of public groundwater supplies and military training ranges. Perchlorates have been shown to compete with iodide, inhibiting thyroid gland function. The presence of polychlorinated organic materials in green-, red-, and blue-light-emitting pyrotechnics are used to effectively color the flame, but are problematic due to their tendencies to form carcinogenic polychlorinated biphenyls, polychlorinated dibenzodioxins, and polychlorinated dibenzofurans when the pyrotechnic formulations are ignited. The presence of barium in green-light-emitting pyrotechnics is necessary to achieve an acceptable green color, but the heavy metal nature of barium and negative health effects associated with barium-containing chemicals is problematic. In an effort to benefit public health and to adequately address environmental concerns facing the commercial fireworks industry and the U.S. military, green-, red-, and blue-light-emitting pyrotechnic illuminants have been developed that do not contain the aforementioned noxious chemicals. While these technologies have been developed and tested by the U.S. military for potential soldier use, its appeal extends to the commercial fireworks industry that is also looking to adopt environmentally friendly technologies in their fireworks displays. Once implemented, this technology is estimated to reduce 300 pounds of perchlorates, 1,500 pounds of barium-based chemicals, and 650 pounds of polychlorinated organic materials from being released into the air annually in military pyrotechnics alone. Due to the large amount of fireworks used commercially, adaptation of these aforementioned technologies by fireworks companies would lead to very large-scale elimination of perchlorates, barium-based chemicals, and polychlorinated organic materials.

**UOP LLC, A  
Honeywell  
Company**

### *A Feedstock Flexible Process to produce Diesel and/or Jet Fuel from Renewable Resources*

UOP has developed catalysts and process technology for a novel chemical route to convert bioderived oils to jet fuel and diesel. This is part of a strategy to sustainably mitigate CO<sub>2</sub> emissions from the aviation, marine, and land transportation sectors via biofuels that can utilize existing fuel infrastructure for delivery, while not requiring modifications to engine technology.

By in-depth understanding of the underlying chemistry, UOP has developed a practical, proven and sustainable solution to produce both diesel and jet fuels from a broad range of bio-feedstock options (including jatropha, camelina, algal oil, animal fats, and used cooking oil) utilizing existing refinery infrastructure, assets and distribution networks. This breakthrough required both new catalysts and process flow schemes, endorsed as novel by the U.S. Patent Office, with 25 patents granted to date and recognized by American Institute of Chemical Engineers' 2010 Sustainable Energy Award.

This technology has now been successfully commercialized in multiple locations and has brought, to date, over 450 million gallons of renewable fuel to the market. In doing so, it has already reduced greenhouse gas emissions in the transportation sector by an estimated 4 million tons of CO<sub>2</sub>.

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Office of Pollution  
Prevention and  
Toxics (7406M)

744F16001  
July 2016  
[www.epa.gov](http://www.epa.gov)